EMULSION COPOLYMERIZATION OF BUTADIENE AND STYRENE AT ELEVATED TEMPERATURES

SUPPLEMENT
STUDIES IN THE SYNTHESIS OF LINEAR POLYBUTADIENE

BY

CAMERON DAVID LEWIS

A. B., University of Buffalo, 1942

A. M., University of Illinois, 1945

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE
UNIVERSITY OF ILLINOIS, 1947

URBANA, ILLINOIS

1947

EMULSION COPOLYMERIZATION OF BUTADIENE AND STYRENE AT ELEVATED TEMPERATURES

SUPPLEMENT
STUDIES IN THE SYNTHESIS OF LINEAR POLYBUTADIENE

BY

CAMERON DAVID LEWIS

A. B., University of Buffalo, 1942

A. M., University of Illinois, 1945

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE
UNIVERSITY OF ILLINOIS, 1947

URBANA, ILLINOIS

1947

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor C. S. Marvel for suggesting and directing these investigations. He also wishes to thank Dr. J. H. Saunders, Dr. Rudolph Deanin, Dr. R. L. Myers, Dr. E. R. Alexander and Dr. L. E. Miller for their many helpful suggestions.

The author is indebted to Mr. Howard Clark for the microanalyses and to Mr. Don Smith and Miss Lois Smith for assistance in experimental work. He is also grateful to Dr. I. M. Kolthoff of the University of Minnesota for the determination of the ratio of 1, 2 and 1, 4 addition in a copolymer and to Mr. E. H. Fohrell for the measurements of surface-film thickness. He desires to thank the Firestone Tire and Rubber Company and the B. F. Goodrich Company for the evaluation of the copolymers.

This work was done under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

R. UNIV. BIBLIOTHEEK LEIDEN

EMULSION COPOLYMERIZATION OF BUTADIENE AND STYRENE AT ELEVATED TEMPERATURES

Introduction

The principal synthetic rubber currently manufactured in the United States is compounded from the butadiene-styrene copolymer commonly designated as GR-S. At the initiation of the government rubber program, emulsion polymerization at a temperature of 50° was chosen as a specification for full-scale commercial production of this copolymer. This temperature represented a compromise, since a lower rate of production would have resulted at lower temperatures and, at temperatures of from 60° to 70°, a polymer of poor quality was usually obtained in the standard recipe.[1]

Subsequently, interest in more rapid production of high-quality synthetic rubber has encouraged further research in polymerizations at temperatures other than 50° and in continuous processes. The feasibility of rapid emulsion copolymerization of butadiene and styrene at temperatures in the neighborhood of 100° has been demonstrated on the laboratory[2] and on the pilot-plant scales.[3] In a continuation of the laboratory studies quantities of 100° copolymer have been prepared for further evaluation in the GR-S recipe, and improvements in the properties of high-temperature copolymers have been sought through the substitution of *n*-butyl mercaptan and of *n*-octyl mercaptan for dodecyl mercaptan in the recipe. Improvement of the polymerization rate has also been sought, with a view to the application of the high-temperature reaction to a continuous process.

Experimental and Discussion

The polymerizations were carried out under closely controlled conditions of time and temperature in lightweight

stainless steel bombs rotated in an oil-bath thermostat. Conversions, benzene solubility, and intrinsic viscosity values for the polymers were determined when reaction time, temperature, and polymerization recipe were varied. The rubber-like properties of compounded and cured copolymers were evaluated and compared with the properties of the standard 50° synthetic rubber. The ratio of 1, 2 and 1, 4 addition and the surface-film thickness were measured for one type of copolymer.

It had been observed[2,3] that the copolymerization of butadiene and styrene occurs rapidly in the standard recipe at high temperatures. In the present studies, average conversions of 63 per cent were obtained in thirty minutes at 100°. Some lack of reproducibility as to conversion was encountered in repeated runs under standardized conditions. The products were largely benzene-insoluble, indicating a comparatively high degree of cross-linking, and the solubility value was subject to some variation during repeated runs. The properties of compounded and cured copolymer prepared in the standard recipe were found to be somewhat inferior to those of standard GR-S.

When sufficient *n*-butyl mercaptan was substituted for dodecyl mercaptan in the standard recipe, the polymerization time was approximately doubled, but the products were soluble in benzene.

When sufficient *n*-octyl mercaptan was substituted for dodecyl mercaptan in the standard recipe, polymerization proceeded at a rate comparable with that obtained in the standard recipe, and the products were soluble in benzene. The properties of compounded and cured soluble copolymer were found to be somewhat inferior to those of standard GR-S.

Indications were obtained that *n*-octyl mercaptan is a better promoter-modifier at high temperatures than either the dodecyl or *n*-butyl homologs. This is in contrast with the relatively poor modifying properties of *n*-octyl mercaptan

in 50° polymerizations.[4] In time-conversion studies using *n*-octyl mercaptan indications were obtained that useful copolymer is not formed in polymerizations of less than twenty-eight minutes' duration.

The *n*-octyl mercaptan-modified copolymer was found to have a ratio of 1, 2 and 1, 4 addition and an extent of chain-branching comparable to the values of these properties in standard GR-S, as indicated respectively by perbenzoic acid titration and by surface-film thickness measurements.

Exploratory polymerizations in an activated recipe in which tetrammino-carbonato-cobaltic nitrate was used as catalyst indicated very rapid polymerization at 81-91°.

BIBLIOGRAPHY

1. Private communication, through the Office of Rubber Reserve, 1942.
2. Rabjohn, Dearborn, Blackburn, Inskeep, Snyder, and Marvel, J. Polymer Sci., in press.
3. Taft, Snyder, and Oates, University of Akron, private communication, through the Office of Rubber Reserve, May 31, 1946.
4. Kolthoff and Harris, J. Polymer Sci., **2**, 49 (1947).

SUPPLEMENT

STUDIES IN THE SYNTHESIS OF LINEAR POLYBUTADIENE

If a butadiene polymer of completely known structure could be obtained, a knowledge of its properties should assist in the establishment of a basis for the correlation of structure with properties for the important butadiene polymers and copolymers.[1] A completely linear polybutadiene of known

steric configuration should be especially useful. Orienting experiments were carried out in two approaches to the synthesis of a linear, largely *trans*-polybutadiene. One approach was concerned with the investigation of methods for the reductive dehalogenation of polychloroprene, which is believed to be essentially linear and largely *trans*.[2] The other approach investigated the possible linear polyaldol condensation of crotonaldehyde,[3] whose configuration is almost exclusively *trans*.[4]

BIBLIOGRAPHY

1. Reynolds, University of Cincinnati, private communication, through the Office of Rubber Reserve, July 5, 1945.
2. Carothers, Williams, Collins, and Kirby, J. Am. Chem. Soc., **53,** 4203 (1931).
3. Smedley, J. Chem. Soc., **99,** 1627 (1911).
4. Young, J. Am. Chem. Soc., **54,** 2498 (1932).

VITA

The author was born in Staunton, Virginia, on June 1, 1920. He attended the parochial schools of Alexandria, Virginia, and Kenmore, New York, and was graduated from Kenmore High School in June, 1938. In September of that year he enrolled in the University of Buffalo, Buffalo, New York, and was graduated in June, 1942, with the degree of Bachelor of Arts in Chemistry. He enrolled in the Graduate School of the University of Illinois in the same month and was granted the degree of Master of Arts in Chemistry in June, 1945. He was employed by the Illinois Geological Survey, Urbana, Illinois, from June, 1942, to July, 1946, first as a Research Assistant and later as an Assistant Chemist. Since July, 1946, he has held a Special Research Assistantship in Chemistry on the Rubber Research Program of the University.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549815_0047